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(54) Title: HERBICIDAL SULFONYL UREA DERIVATIVES (57) Abstract <p>The present invention relates to novel sulfonyl urea derivatives of formula (I) having erythro-type stereoisomer as herbicides for treatment of pre-emergence and/or post-emergence, their use and composition as agriculturally suitable herbicides, wherein, P and Q, as equivalent or different group respectively, are CH or N, and present as aromatic ring including P and Q as benzene or pyridine ring; R is H, (a) or (b) group, wherein R^a is C₁ ~ C₄ alkyl, C₁ ~ C₃ haloalkyl, C₂ ~ C₄ alkenyl or C₂ ~ C₄ alkynyl group, wherein X^a is O, S, NH or NR^a group; R' is H or CH₃ group; and X and Y are independently halogen atom, C₁ ~ C₂ alkyl, C₁ ~ C₂ alkoxy or C₁ ~ C₂ haloalkoxy group.</p> <div style="text-align: center;"> <p style="text-align: right;">(I)</p> </div>		

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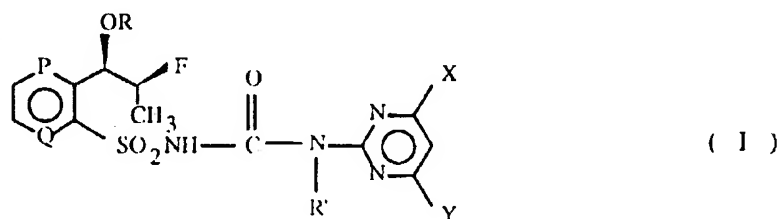
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HERBICIDAL SULFONYL UREA DERIVATIVES¹

BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates to novel sulfonyl urea derivatives of the following formula (I) having erythro-type stereoisomer as herbicides for treatment of pre-emergence and/or post-emergence, their use and composition as agriculturally suitable herbicides.



wherein,

P and Q, as equivalent or different group respectively, are CH or N, and present as aromatic ring including P and Q as benzene or pyridine ring ;

15 R is H, $R^a - \overset{\overset{\text{O}}{\parallel}}{\text{C}} -$ or $R^a - X^a - \overset{\overset{\text{O}}{\parallel}}{\text{C}} -$ group, wherein R^a is $C_1 - C_4$ alkyl, $C_1 - C_3$ haloalkyl, $C_2 - C_4$ alkenyl or $C_2 - C_4$ alkynyl group, wherein X^a is O, S, NH or NR^a group;

R' is H or CH_3 group; and

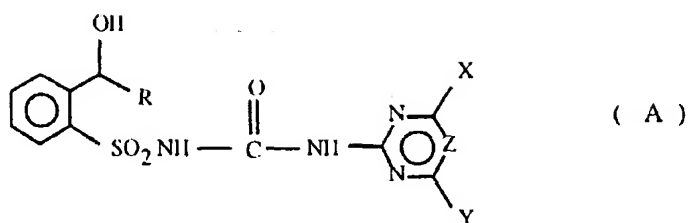
20 X and Y are independently halogen atom, $C_1 - C_2$ alkyl, $C_1 - C_2$ alkoxy or $C_1 - C_2$ haloalkoxy group.

Description of the Prior Art

It is publicly well-known that sulfonyl urea derivatives possess a herbicidal activity. Such examples containing sulfonyl urea are;

- (1) Korea Patent publication No. 93-9825 discloses the compound having the following formula(A)

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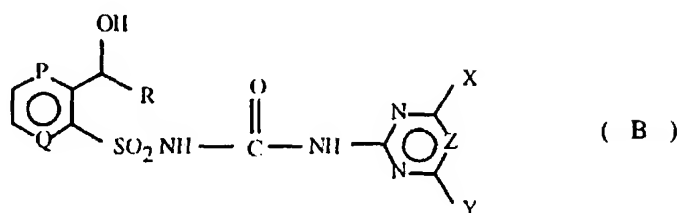
wherein,

R is haloalkyl ;

X and Y are independently CH₃, OCH₃ or Cl etc. ;

5 Z is CH or N.

- (2) Korea Patent publication No. 93-9507 discloses the compound having the following formula(B)



10 wherein,

R, X, Y and Z are as previously defined,

P and Q are differently N or CH.

If R group of the above formula(A) and (B) includes asymmetric carbon atom,
 15 then the above compound has two stereoisomers which are threo- and erythro-type by reason of two asymmetric carbon atom. But herbicidal activity and selectivity of the above stereoisomers have been not disclosed.

SUMMARY OF THE INVENTION

20 The object of the present invention is to provide novel sulfonyl urea derivatives having very prominent herbicidal activities toward rice and wheat and also possess a good selectivity for annual and perennial weed, especially a barnyard grass.

Another object of this invention is to provide herbicidal compositions containing said derivatives as active compounds.

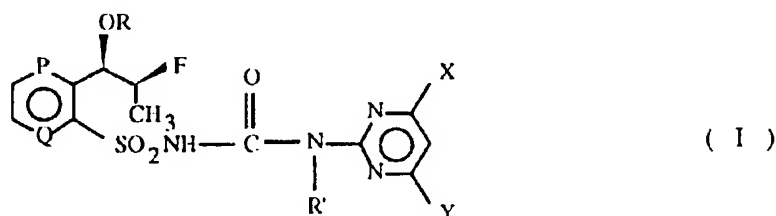
BRIEF DESCRIPTION OF THE INVENTION

Fig. 1 is stereoconfiguration based upon X-ray crystallography analysis of the compound manufactured by EXAMPLE 1.

Fig. 2 is stereoconfiguration based upon X-ray crystallography analysis of the compound manufactured by EXAMPLE 9.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to herbicidal sulfonyl urea derivatives with substituent of erythro-type stereoisomer having the following formula(I), which have herbicidal selectivity toward rice and wheat, and their agriculturally suitable salts.



wherein,

P, Q, R, R', X and Y are as previously defined.

A preferred group of erythro-type stereoisomer of the above formula(I), in view of a strong activity and a good selectivity is as follows :

- (1) Benzene(P and Q are independently CH)
- (2) Pyridine(P is N, and Q is CH)
- (3) R is hydrogen atom
- (4) R' is hydrogen atom
- (5) R is acetyl group
- (6) X and Y are methoxy group.

These compounds can easily control barnyard grass as well as a perennial weed causing trouble for rice and can be used agriculturally as herbicidal composition for rice. Especially the following compounds have a good selectivity for rice :

- 5 Erythro *N*-[(4,6-dimethoxy-pyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1-hydroxy-*n*-propyl)-3-pyridinesulfonamide,
Erythro *N*-[(4,6-dimethoxy-pyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1-hydroxy-*n*-propyl)-benzenesulfonamide, etc..

The erythro-type compounds of the above formula(I) according to the present invention have more prominent herbicidal activity than threo-type or mixture of erythro-
10 and threo-type. Furthermore, the erythro-type compounds of the above formula(I) may be used as herbicides or active ingredient of herbicidal composition because of a good selectivity for rice and wheat.

A pure compound of erythro-type having the above formula(I) according to the present invention can be prepared by reactions described in herein below, but should not
15 be constructed to be limited hereto.

The compound of the above formula(I), in which R is hydrogen atom, can be obtained by hydrolyzing the compound of the above formula(I), where R is acyl group such as acetyl group, in present of alkali.

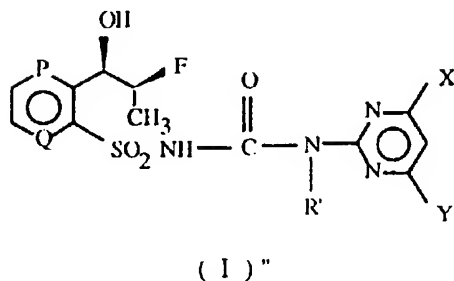
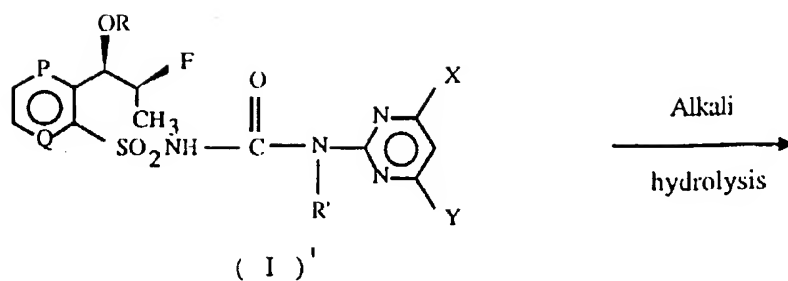
In order to hydrolyze the above acyl group, alkali such as LiOH, KOH, NaOH,
20 Li_2CO_3 , Na_2CO_3 , K_2CO_3 , etc., preferably LiOH, may be used.

The above hydrolysis reaction is carried out under water or organic solvent, as a mixture of water with unreacting solvent such as methanol, ethanol, acetone, tetrahydrofuran, dimethylformamide, etc., or solvent alone. The hydrolysis occurs at the temperature of 0 ~ 80 °C in a reaction time of 1-24 hours, and then the obtained
25 product may be easily separated by acidifying with aqueous HCl solution.

As an other process, after acidifying, the obtained product is extracted with methylene chloride, ethyl acetate, etc. and then concentrated to obtain the final product. If necessary, a pure product can be obtained by purification using HPLC.

The hydrolysis in the above reaction is carried out as shown in the following
30 reaction scheme.

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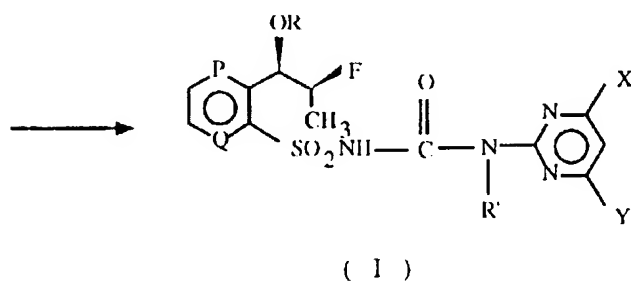
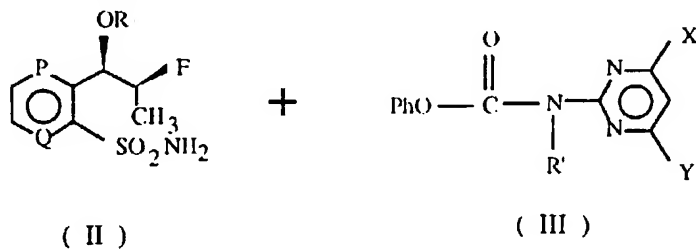


wherein,

P, Q, R', X and Y are respectively defined as the above formula (I), and

5 R is defined as the above formula (I) except of hydrogen atom.

Also, the compounds of the above formula (I) according to the present invention can be prepared by reacting the erythro-type compound having the following formula (II) with the compound having the following formula (III).



10

wherein,

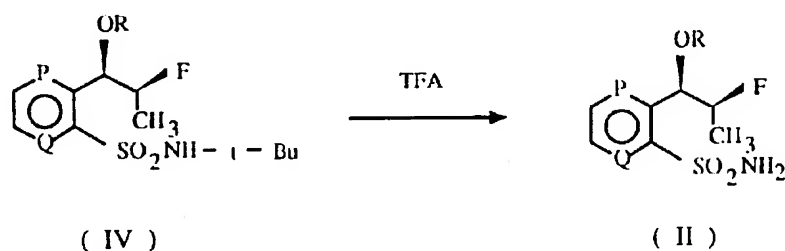
P, Q, R, R', X and Y are respectively defined as the above formula(I).

In the above reaction, unreacting solvent such as tetrahydrofuran, acetone,
5 acetonitrile, dioxane, methylene chloride, toluene, butanone, pyridine,
dimethylformamide, etc., may be used.

The reaction may be preferably carried out under strong base such as DBU or
DABCO, etc. in a small quantity at the temperature of 20-80 °C. The above reaction is
referred to in U.S. patent No. 4,443,245 and thereafter the desired product can be
10 obtained by acidifying by the method mentioned in European Patent No. 44,807. If
necessary, a pure product can be obtained by purification by HPLC. Said, DBU
represents 1,8 - diazabicyclo[5.4.0] undec-7-ene, and DABCO represents 1,4-diazabicyclo
[2.2.2]octane.

Also, the compound of the formula(III) used for preparing the above formula(I)
15 can be easily obtained by the prior art.

On the other hand, the erythro-type of the above formula(II) can be prepared by
the following reaction scheme.



20 wherein,

P, Q and R are respectively defined as the above.

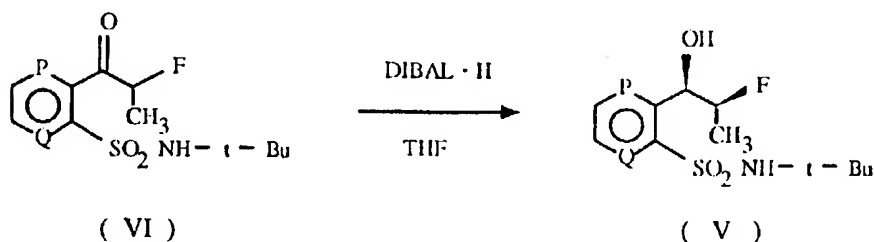
In the above reaction, the primary sulfonamide of erythro-type having the above
formula(II) can be prepared by treating *N*-*t*-butylsulfonamide of the above formula(IV)
25 with an acid such as trifluoroacetic acid (TFA) at the temperature of 0-50 °C.

Also, the erythro-type of the above formula(IV) used in the above reaction can be

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prepared by common acylation of the following formula(V). The pure erythro-type of the above formula(IV) can be separated from mixture of threo- and erythro-type by purification such as column chromatograph, HPLC or prep-TLC.

The compound of the following formula(V) can be prepared by selective reduction
 5 of the compound of the following formula(VI) with selective reductant such as diisobutylaluminum hydride.



wherein,

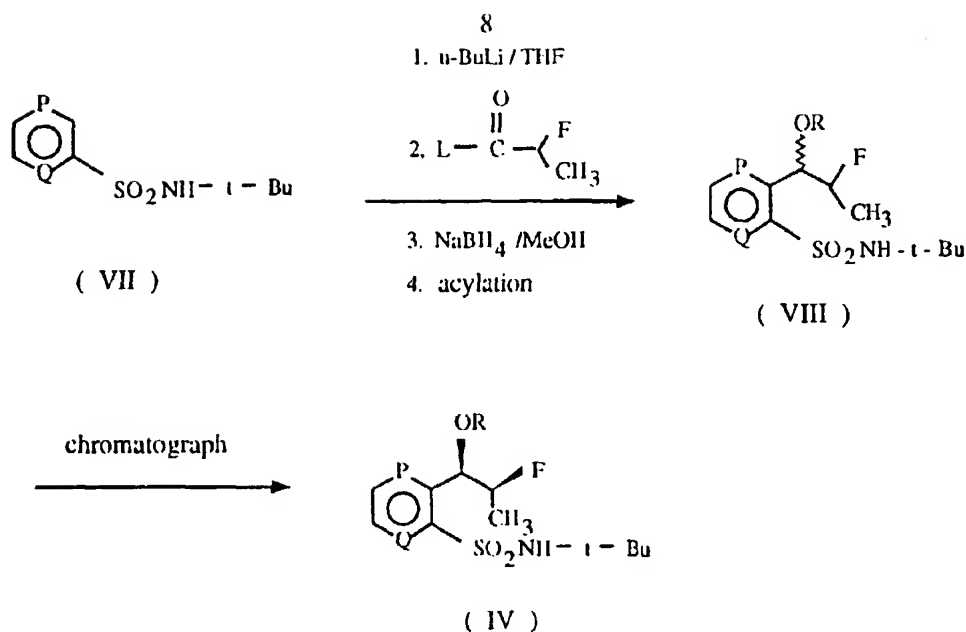
10 P and Q are respectively defined as the above.

DIBAL · H is diisobutylaluminum hydride.

In the above reaction, preferably P is N and Q is CH.

The pure erythro-type of the above formula(V) can be easily purified using column
 15 chromatograph.

The compound of the above formula(IV) can also be prepared by another process as shown in the following reaction.



wherein,

P and Q are respectively defined as the above formula(I),

R is defined as the above formula(I) except of hydrogen atom,

5 L is alkoxy, $\text{N}(\text{CH}_3)_2$ or $\text{NCH}_3(\text{OCH}_3)$, etc..

The above reaction process has been disclosed in Korea Patent Application No. 91-3704 and No. 91-3014. *n*-Butyl lithium of 2 equivalents are added in the compound of the above formula(VII) in THF solvent for 1~24 hours at $-80 \sim +30^\circ\text{C}$ to

10 obtain dilithio salt, and then $\text{L}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CHF}-\text{CH}_3$ is added at $-70 \sim -80^\circ\text{C}$ to obtain ketone compound. Hydroxy compound is obtained by reduction of the ketone compound with NaBH_4 , and then the compound of formula (VII) wherein R is acetyl group is obtained
 15 by acylation under acetic anhydride, DMAP and pyridine.

The pure erythro-type of the above formula (IV) can be easily obtained by separation and purification techniques such as HPLC, column chromatograph, prep-TLC, etc..

On the other hand, salts of the compound of the above formula(I) which are also useful as herbicide, can be prepared by various methods according to prior art. For
 20 example, metal salts of the compound can be prepared by reacting the above formula(I)

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compound with strong basic anion, e.g. alkali or alkaline earth metal solution having hydroxyl group, alkoxide or carbonate, and also quaternary amine salt alike.

A salt of the formula(I) compound may also be obtained by cation exchange.

The cation exchange can be carried out by directly reacting a solution containing cation

5 for exchange with the solution of salt of formula(I), for example aqueous solution of alkali metal or quaternary amine salt. This method is useful when the desirable salt is water soluble, especially sodium, potassium or calcium salt.

The above manufacturing methods are summarized briefly, and the methods can be carried out easily by a person skilled in the technical field for manufacturing sulfonyl
10 urea or organic composition.

The compounds of the above formula(I) according to the present invention may be specified as the following Table 1.

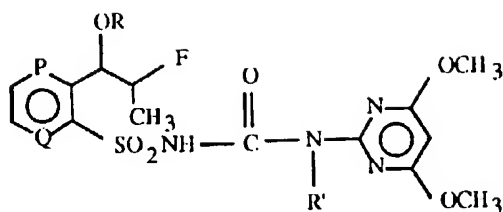
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Table 1.



	Isomer	P	Q	R	R'	m.p.(°C)
5	erythro	CH	CH	H	H	166 - 168
	erythro	CH	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_3 \end{array}$	H	191 - 193
	erythro	N	CH	H	H	151 - 153
10	erythro	N	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_3 \end{array}$	H	218 - 220
	erythro	CH	N	H	H	
15	erythro	CH	N	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_3 \end{array}$	H	
20	erythro	CH	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_2\text{CH}_3 \end{array}$	H	151-153
25	erythro	N	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_2\text{CH}_3 \end{array}$	H	
	erythro	CH	N	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_2\text{CH}_3 \end{array}$	H	
30						

35

5	Isomer	P	Q	R	R'	m.p.(°C)
	erythro	CH	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_2\text{CH}_2\text{CH}_2 \end{array}$	H	
10	erythro	N	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_2\text{CH}_2\text{CH}_2 \end{array}$	H	
15	erythro	CH	N	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_2\text{CH}_2\text{CH}_2 \end{array}$	H	
20	erythro	CH	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_3 \end{array}$	H	186 - 192
25	erythro	N	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_3 \end{array}$	H	
	erythro	CH	N	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_3 \end{array}$	H	
30	erythro	CH	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_2\text{CH}_3 \end{array}$	H	168 - 170
35	erythro	N	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_2\text{CH}_3 \end{array}$	H	
40	erythro	CH	N	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_2\text{CH}_3 \end{array}$	H	
45	erythro	CH	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_2\text{CH}=\text{CH}_2 \end{array}$	H	

	Isomer	P	Q	R	R'	m.p.(°C)
5	erythro	N	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_2\text{CH}=\text{CH}_2 \end{array}$	H	
10	erythro	CH	N	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_2\text{CH}=\text{CH}_2 \end{array}$	H	
15	erythro	CH	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_2\text{C}\equiv\text{CH} \end{array}$	H	
20	erythro	N	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_2\text{C}\equiv\text{CH} \end{array}$	H	
25	erythro	CH	N	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_2\text{C}\equiv\text{CH} \end{array}$	H	
	erythro	CH	CH	H	CH ₃	139 - 140
	erythro	CH	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_3 \end{array}$	CH ₃	162- 164
	erythro	N	CH	H	CH ₃	
30	erythro	N	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_3 \end{array}$	CH ₃	
	erythro	CH	N	H	CH ₃	
35	erythro	CH	N	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_3 \end{array}$	CH ₃	
40						
45						

	Isomer	P	Q	R	R'	m.p.(°C)
5	threo	CH	CH	H	H	189 - 191
	threo	CH	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_3 \end{array}$	H	194 - 196
10	threo	N	CH	H	H	173 - 175
	threo	N	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_3 \end{array}$	H	190 - 192
15	threo	CH	N	H	H	
	threo	CH	N	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_3 \end{array}$	H	
20	threo	CH	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_2\text{CH}_3 \end{array}$	H	
25	threo	N	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_2\text{CH}_3 \end{array}$	H	
30	threo	CH	N	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_2\text{CH}_3 \end{array}$	H	
	threo	CH	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_2\text{CH}=\text{CH}_2 \end{array}$	H	
35	threo	N	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_2\text{CH}=\text{CH}_2 \end{array}$	H	

40

	Isomer	P	Q	R	R'	m.p.(°C)
5	threo	CH	N	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_2\text{CH}=\text{CH}_2 \end{array}$	H	
10	threo	CH	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_3 \end{array}$	H	
15	threo	N	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_3 \end{array}$	H	
	threo	CH	N	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_3 \end{array}$	H	
20	threo	CH	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_2\text{CH}_3 \end{array}$	H	
25	threo	N	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_2\text{CH}_3 \end{array}$	H	
30	threo	CH	N	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_2\text{CH}_3 \end{array}$	H	
35	threo	CH	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_2\text{CH}=\text{CH}_2 \end{array}$	H	
	threo	N	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_2\text{CH}=\text{CH}_2 \end{array}$	H	
40	threo	CH	N	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_2\text{CH}=\text{CH}_2 \end{array}$	H	
45						
50						

	Isomer	P	Q	R	R'	m.p.(°C)
5	threo	CH	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_2\text{C}\equiv\text{CH} \end{array}$	H	
10	threo	N	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_2\text{C}\equiv\text{CH} \end{array}$	H	
15	threo	CH	N	$\begin{array}{c} \text{O} \\ \parallel \\ \text{COCH}_2\text{C}\equiv\text{CH} \end{array}$	H	
	threo	CH	CH	H	CH ₃	
20	threo	CH	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_3 \end{array}$	CH ₃	
25	threo	N	CH	H	CH ₃	
	threo	N	CH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_3 \end{array}$	CH ₃	
30	threo	CH	N	H	CH ₃	
35	threo	CH	N	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CCH}_3 \end{array}$	CH ₃	

The sulfonyl urea derivatives having erythro-type stereoisomer of the above formula(I) according to the present invention are useful as herbicides. The applied method is given below.

5 [Utility]

The compounds according to the present invention represent very high activity as pre- or post- emergence herbicides and water surface treatment or leaf treatment herbicides for rice.

The used amount of compound of the present invention is decided by several
10 factor, that is, kinds of weeds, climate or weather, formulations selected, the applied method or the size of weed etc.

The active ingredients can be generally used from 1 g to 1 kg per hectare. Smaller quantity may be used in soil containing low organic matter or sandy soil, young plant or when the herbicidal effect is need of short-termed duration.

15 The compounds according to the present invention are especially effective as ingredient for control of weed in rice and wheat field, especially leaf-width weed, graminaceae weed and annual or perennial weed. The compounds are particularly effective for control of barnyard grass.

The list of weeds controllable by the compounds of the present invention is given
20 below.

[the list of weeds]

dicotyledon weeds genus:

Sinapis, Lepidium, Galium, Stellaria, Matricaria, Anthemis, Galinsoga,
25 Chenopodium, Urtica, Senecio, Amaranthus, Portulaca, Xanthium, Convolvulus, Ipomoea, Polygonum, Sesbania, Ambrosia, Cirsium, Carduus, Sonchus, Solanum, Rorippa, Rotala, Lindemia, Lamium, Veronica, Arbutilon, Emex, Datura, Viola, Galeopsis, Papaver, Centaurea.

monocotyledon weeds genus:

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Echinochloa, Setaria, Panicum, Digitaria, Phleum, Poa, Festuca, Eleusine, Brachiaria, Lolium, Bromus, Avena, Cyperus, Sorghum, Agropyron, Cynodon, Monochoria, Fimbristylis, Sagittaria, Eleocharis, Scirpus, Paspalum, Dactyloctenium, Agrostis, Alopecurus, Apera, Heteranthera, Leptochloa.

- 5 The compounds of the present invention can be used as alone or in combination with two, three or four additives with other herbicides. The appropriate herbicides for mixed-using with the compounds of the present invention are given below. It is particularly useful for control of weeds to use the mixture of the compounds of the present invention and the below herbicides.

10 Common Name

acetochlor	acifluorfen
AC 252,214	AC 263,499
acrolein	alachlor
ametryn	amitrole
15 AMS	asulam
assure	atrazine
BAS-514	barban
benefin	bensulfuron methyl
bensulide	bentazon
20 benzoafluor	benzoylprop
bifenox	bromacil
bromoxynil	butachlor
buthidazole	butralin
butylate	cacodylic acid
25 CDAA	CDEC
CGA 82725	CH-83
chloramben	chlorbromuron
chlorimuron ethyl	chloroxuron
chlorpropham	chlorsulfuron

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	chlortoluron	cinmethylin
	clethodim	clomazone
	cloproxydim	clopyralid
	CMA	cyanazine
5	cycloate	cycluron
	cyperquat	cyprazine
	cyprazole	cypromid
	dalapon	dazomet
	DCPA	desmediphan
10	desmetryn	diallate
	dicamba	dichlorbenil
	dichlorprop	dichlofop
	diethatyl	difenzoquat
	dinitramine	dinoseb
15	diphenamid	dipropetryn
	diquat	diuron
	DNOC	DOWCO 453 ME
	DPX-M6316	DSMA
	endothall	EPTC
20	ethalfluralin	ethofumesate
	express	fenac
	fenoxapropethyl	fenuron
	fenuron TCA	flamprop
	fluzifop	fluzifopbutyl
25	fluzifop-P	fluchloralin
	fluometuron	fluorochloridone
	fluorodifen	fluoroglycofen
	fluridone	fomesafen
	fosamine	glyphosate

	haloxyfop	19	harmony
	hexaflurate		hexazinone
	HW-52		imazamethabenz
	imazapyr		imazaquin
5	imazethapyr		ioxynil
	isopropalin		isoproturon
	isouron		isoxaben
	karbutilate		lactofen
	lenacil		linuron
10	MAA		MAMA
	MCPA		MCPB
	mecoprop		melfluidide
	methalpropalin		methabenzthiazuron
	metham		methazole
15	methoxuron		metolachlor
	metribuzin		metsulfuron methyl
	MH		molinate
	monolinuron		monuron
	monuron TCA		MSMA
20	My-93		napropamide
	naproanilide		naptalam
	neburon		nitratin
	nitrofen		nitrofluorfen
	norea		norflurazon
25	NTN-801		oryzalin
	oxadiazon		oxyfluorfen
	paraquat		pebulate
	pendimethalin		perfluidone
	phenmedipham		picloram

	PPG-1013	20	pretilachlor
	procyazine		profluralin
	prometon		prometryn
	pronamide		propachlor
5	propanil		propazine
	propham		prosulfalin
	pyrnachlor		pyrazon
	pyrazolate		quizalofop
	quizalofop ethyl		SC-2957
10	sechumeton		sethoxydim
	siduron		simazine
	SL-49		sulfometuron methyl
	TCA		tebuthiuron
	terbacil		terbuchlor
15	terbutylazine		terbutol
	terbutryn		thiameturon methyl
	thiobencarb		triallate
	triclopyr		tridiphane
	trifluralin		trimeturon
20	2,4-D		2,4-DB
	vernolate		X-52
	xylachlor		Saturn
	KH-218		NSK-850
	Pyrazoxyfen		Dimension
25	CH-900		Metenacet
	TSH-888		Dymron
	Dimepiperate		Isoxapyrifos
	Phenobenzuron		JC-940
	Esprocab		Methylbencab

	Phenopylate	21	Benfuresate
	S-275		Quinclorac
	Londax		NC-311
	TH-913		HW-52
5	DEH-112		SKH-301
	Bromobutide		BAS517H
	RE45601		RE36290
	RO173664		HOE075032
	ICIA6051		DPX ^a 7881
10	MW801		CGA136872
	DPXV9360		DPXE9636
	SL950		ICIA02957
	CGAI42464		MY15
	MON7200		WL95481
15	DPXY6202		MON15100
	SL160		ICIA0224
	LS83556		BAS518H
	CGA131036		DPXL5300
	HOE70542		ICIA0604
20	ICIA0574		LS846215

[Formulation]

Formulations for the use of the compounds of formula(I) can be prepared in conventional ways. They include dusts, granules, pellets, solutions, suspensions, emulsions, wettable powders, emulsifiable concentrates and the like. Many of these may be applied directly.

Sprayable formulations can be prepared in suitable media and used at spray volumes of from a few liters to several hundred liters per hectare. High strength compositions are primarily used as intermediates for further formulation. The

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formulations, broadly, contain about 0.1% to 98.9% by weight of active ingredient(s) and at least one of (1) about 0.1% to 20% surfactant(s) and (2) about 1% to 99.8% solid or liquid inert diluent(s) are recommended. More specially, the formulations will contain these ingredients in the following approximate proportions:

5

Table 2.

10	Formulations	Weight Percent(%)		
		Active Ingredient	Diluent	Surface Active Agent
	Wettable Powders	20-90	1-74	1-10
	Oil Suspension, Emulsions, Solution Emulsifiable Concentrates	3-50	40-95	0.1-15
15	Aqueous Suspension	10-50	40-84	1-20
	Dusts	1-25	70-98.9	0.1-5
	Granules and Pellets	0.1-95	5-99.8	0.1-15
	High strength Composition	90-98.9	1-10	0.1-2

20 Lower or higher levels of active ingredient can, of course, be present depending on the intended use and the physical properties of the compound. Higher ratios of surface active agent to active ingredient are sometimes desirable, and are achieved by incorporation into the formulation or by tank mixing.

Typical solid diluents are mentioned in the writings of Watkins, et al. ("Handbook
25 of Insecticide Dust Diluents and Carrier" 2nd Ed., Dorland Books, Caldwell, N.J.) and other solid diluents can be used.

The more absorptive diluents are preferred for wettable powders and the denser ones for dusts.

Typical liquid diluents and solvents are mentioned in the writings of Marsden
30 ("Solvents Guide", 2nd Ed., Interscience, New York, 1950).

Solubility under 0.1% is preferred for concentrated suspension; concentrated

solution is preferably stable against phase separation at 0°C.

The surface active agents and their using method is mentioned in the writings of McCutcheon (McCutcheon's Detergents and Emulsifiers Annual, Mc Publishing Corp., Ridgewood, N. J.) and Sisely et al. (Sisely and Wood, "Encyclopedia of Surface Active Agents", Chemical Publishing Co., Inc., New York, 1964).

All the above formulations may contain a small amount of additives to reduce foaming, caking, corrosion and the growth of microorganisms.

The preparation methods of such compositions are well known. A solution can be made only by blending properties and a fine solid composition by blending and pulverizing.

Suspension agents can be made by wet milling method (U.S. Patent No. 3,060,084) and granules and pellets can be made by spraying the active ingredient on preformed granular carrier, or by Agglomeration method (J.E. Browing, "Agglomeration" Chemical Engineering, Dec. 4, 1967, pp147 / "Perry's Chemical Engineer's Handbook," 5th Ed., McGraw-Hill, New York, 1973, pp 8-57ff).

For further information regarding the art of formulations, see for example: US patent No. 3,235,361 / 3,309,192 / 2,891,855, G. C. Klingman, "Weed Control as a Science", John Wiley and Sons, Inc., New York, 1961, pp.81-96 / J. D. Fryer and S. A. Evans, "Weed Control Handbook", 5th Ed., Blackwell Scientific Publications Oxford, 1968, pp.101-103.

The compounds of the present invention can be used independently and may be used in combination with any other commercial herbicides. To specify some more the manufacturing and using of the compounds of the present invention, the detailed examples are described below.

EXAMPLE 1

Erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-*t*-butyl-benzenesulfonamide.

Erythro *N*-*t*-butyl-2-(2-fluoro-1-hydroxy-*n*-propyl)-benzenesulfonamide (3.5 g) was dissolved in 50 ml of methylene chloride and herein acetic anhydride (1.25 ml),

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pyridine(1.1 ml) and *N,N*-dimethyl aminopyridine(0.12 g) were added. After stirring for 1 hour, the reacting solution was diluted with methylene chloride and washed with 5% hydrochloric acid solution. The separated organic layer was dried with magnesium sulfate, filtered and concentrated. And then the obtained residue was chromatographed
 5 through silicagel using 1 : 3(v/v) solution of ethyl acetate/hexane to afford 3.7 g of the desired product(white solid).

m.p. : 134 ~ 135 °C

¹H NMR(200MHz, CDCl₃) : δ 1.25(s, 9H), 1.36(dd, 3H, *J*_{H-H}=6.4Hz, *J*_{H-F}=
 25.3Hz), 2.17(s, 3H), 4.86-5.22(m, 1H), 5.47(brs,
 10 1H), 6.68(dd, 1H, *J*_{H-H}=3Hz, *J*_{H-F}=18.6Hz),
 7.41-7.71(m, 3H), 8.04-8.12(m, 1H).

IR(KBr) ν (C=O) 1715 cm⁻¹

Crystal data of product prepared by the above EXAMPLE 1 is the following.

Crystal data

15 Molecular Formula : C₁₃H₂₂FNO₄S
 Measured Density(D_m) : 1.3 Mg m⁻³
 Molecular Weight(M_r) : 331.4
 Used Wave Length(λ) : 0.71069 Å
 Crystal System : monoclinic system
 20 No. of diffraction data used in measuring lattice constant : 25
 Size of unit cell
 a = 13.693(6) Å
 b = 14.731(15) Å
 c = 8.737(5) Å
 25 β = 106.51(5) Å
 Volume of unit cell (V) : 1690(1) Å³
 Independent Molecularity(Z) : 4
 Calculating Density(D_x) : 1.303 Mg m⁻³

	25
Hygroscopic Coefficient(μ)	: 1.74 mm^{-1}
Experimental temperature	: 299 K
Size of crystal used in measuring	: $0.3 \times 0.2 \times 0.2 \text{ mm}$
Color	: Colorless
5 Crystal source	: obtained on synthesizing

Data Collection

	Used Diffractometer	: CAD-4 diffractometer made in Netherland Enraf-Nonius company
10	Maximum angle of Scan	: $\theta_{\text{max}} = 24^\circ$
	Scanning Method	: $\omega/2\theta$ scans
	Range of Miller Index	: $h=-15 \rightarrow 15 \quad k=0 \rightarrow 16 \quad l=0 \rightarrow 9$
	Absorption Correction Method	: did not correct.
	measuring method	: 3 of standard data were confirmed
15		every time diffraction data was measured.
	Change of standard data on measuring	: no change
	No. of Measured Data	: 2549
	No. of Independent Data	: 2549
	No. of measured data in significant having threefold of standard deviation	
20		: 2337 [$F > 3\sigma(F)$]

Refinement

	Data used in refining	: F
	Refined parameter	:
	non-hydrogen atom	: atomic coordinates x,y,z and anisotropic temperature factor (u_{ij})
25	hydrogen atom	: isotropic temperature factor (u)
	hydrogen atom coupled nitrogen[H(N)]	: atomic coordinates x,y,z and isotropic temperature factor (u)
	No. of parameter refined by the minimum square method	: 224
30	Final Reliability factor(R)	: 0.0598

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Sequency of refining process variables by the minimum square method (S)

: 3.5233

Manimum differential-composite electron density(ΔP_{\max}) : $0.481 \text{ e } \text{\AA}^{-3}$ Minimum differential-composite electron density(ΔP_{\min}) : $0.349 \text{ e } \text{\AA}^{-3}$ 5 No. of data used in refining : 2337 [$F > 3\sigma(F)$]

Atomic scattering factor used in X-ray crystallography is described in the Table 3
and stereoconfiguration of innermolecular atoms are given in Figure 1.

10

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25

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Table 3.

	Atoms	x	y	z	Ueq
	S	0.2176(1)	0.3425(0)	0.7251(1)	0.040
5	F	0.0756(2)	0.6606(1)	0.8577(3)	0.083
	O(1)	0.2426(2)	0.6366(1)	0.7567(3)	0.052
	O(2)	0.3216(2)	0.5628(2)	0.6045(4)	0.083
	O(3)	0.2209(2)	0.2488(1)	0.7683(3)	0.058
	O(4)	0.1302(1)	0.3754(1)	0.6074(2)	0.051
10	N	0.3128(2)	0.3635(2)	0.6569(3)	0.045
	C(1)	0.2312(2)	0.4071(2)	0.9026(3)	0.039
	C(2)	0.2183(2)	0.5022(2)	0.9026(3)	0.037
	C(3)	0.2415(2)	0.5461(2)	1.0485(4)	0.052
	C(4)	0.2731(3)	0.4985(3)	1.1913(4)	0.061
15	C(5)	0.2813(3)	0.4053(3)	1.1882(4)	0.061
	C(6)	0.2616(2)	0.3593(2)	1.0443(4)	0.053
	C(7)	0.1759(2)	0.5586(0)	0.7527(4)	0.043
	C(8)	0.0707(2)	0.5970(2)	0.7359(4)	0.052
	C(9)	-0.0067(3)	0.5269(3)	0.7416(5)	0.066
20	C(10)	0.3137(3)	0.6290(2)	0.6793(4)	0.050
	C(11)	0.3779(3)	0.7120(3)	0.6955(5)	0.070
	C(12)	0.4207(2)	0.3314(2)	0.7215(4)	0.057
	C(13)	0.4770(3)	0.3671(4)	0.6105(5)	0.097
	C(14)	0.4689(4)	0.3677(7)	0.8839(6)	0.162
25	C(15)	0.4217(5)	0.2279(4)	0.787(12)	0.191

EXAMPLE 2

Threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-*t*-butyl-benzenesulfonamide

From threo *N*-*t*-butyl-2-(2-fluoro-1-hydroxy-*n*-propyl)-benzenesulfonamide (6 g) was obtained 6.4 g of the desired product (white solid) using the same method of

5 EXAMPLE 1.

m.p. : 126 ~ 127 °C

¹H NMR(200MHz, CDCl₃) : δ 1.23(s, 9H), 1.36(dd, 3H, J_{H-H}=6.4Hz, J_{H-F}=23.6Hz),
2.18(s, 3H), 4.73-5.11(m, 1H), 5.54(brs, 1H),
6.49(dd, 1H, J_{H-H}=3.8Hz, J_{H-F}=21.6Hz),
7.41-7.69(m, 3H), 8.02-8.11(m, 1H).

10 IR(KBr) ν (C=O) 1715 cm⁻¹

EXAMPLE 3

Erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-benzenesulfonamide

15 Erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-*t*-butyl-benzenesulfonamide (3.7 g) was dissolved in trifluoroacetic acid(20 ml) after stirring for 24 hours at room temperature was concentrated under vacuum and residue solution was diluted with methylene chloride and washed with 5% NaHCO₃ solution.

The organic layer was dried with magnesium sulfate, filtered and concentrated.
20 and then the concentrated solution was column chromatographed using eluate of ethyl acetate/hexane to afford 2.3 g of the desired product (white solid).

m.p. : 105 ~ 107 °C

¹H NMR(200MHz, CDCl₃) : δ 1.33(dd, 3H, J_{H-H}=6.4Hz, J_{H-F}=24.6Hz),
2.18(s, 3H), 4.85-5.23(m, 1H), 5.55(brs, 2H),
25 6.53-6.68(m, 1H), 7.46-7.75(m, 3H),
8.06-8.13(m, 1H).

EXAMPLE 4

Threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-benzenesulfonamide

The desired product 3.9 g(white solid) was obtained by the same method of
30 EXAMPLE 3 from threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-*t*-butyl-benzenesulfonamide

(6.4 g).

m.p. : 126 ~ 128 °C

¹H NMR(200MHz, CDCl₃) : δ 1.36(dd, 3H, J_{H-H}=6.4Hz, J_{H-F}=24.2Hz),

2.18(s, 3H), 4.75-5.12(m, 1H), 5.57(brs, 2H),

5 6.38-6.53(m, 1H), 7.46-7.66(m, 3H),

8.06-8.13(m, 1H).

EXAMPLE 5

Erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-[(4,6-dimethoxypyrimidin-2-yl)-aminocarbonyl]-benzenesulfonamide [Compound No. 4]

10 Erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-benzenesulfonamide (2.3 g) was dissolved in 20 ml of acetonitrile and herein 2.3 g of phenyl (4,6-dimethoxy pyrimidin-2-yl) carbamate was added at room temperature. 1 ml of DBU was slowly added dropwised. The reacting solution was stirred for 30 minutes and diluted with 100 ml of methylen chloride. Washed with 50 ml of 5% hydrochloric acid solution and 50 ml
15 of water, the organic layer was dried with magnesium sulfate, filtered and concentrated. The obtained residue was treated with ethyl acetate/hexane/ethylether to afford 2.9 g of the desired product (white solid).

m.p. : 191 ~ 193 °C

¹H NMR(200MHz, CDCl₃) : δ 1.33(dd, 3H, J_{H-H}=6.4Hz, J_{H-F}=24.6Hz),

20 2.04(s, 3H), 3.96(s, 6H), 4.86-5.25(m, 1H),

5.80(s, 1H), 6.70-6.82(m, 1H), 7.18-7.70(m, 4H),

8.30-8.40(m, 1H), 13.15(brs, 1H).

EXAMPLE 6

Threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-[(4,6-dimethoxypyrimidin-2-yl)amino-
25 carbonyl]-benzenesulfonamide [Compound No. 5]

5.3 g of the desired product was obtained using the same method of EXAMPLE 5 from 3.9 g of threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-benzenesulfonamide.

m.p. : 194 ~ 196 °C

¹H NMR(200MHz, CDCl₃) : δ 1.33(dd, 3H, J_{H-H}=6.4Hz, J_{H-F}=24.2Hz),

30 2.04(s, 3H), 3.96(s, 6H), 4.80-5.14(m, 1H),

30
 5.80(s, 1H), 6.42-6.62(m, 1H), 7.23-7.70(m, 4H),
 8.27-8.37(m, 1H), 12.95(brs, 1H).

EXAMPLE 7

Erythro *N*-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1-hydroxy-*n*-propyl)-benzenesulfonamide [Compound No. 1]

Erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-benzenesulfonamide (2.9 g) was dissolved in 60 ml of tetrahydrofuran and herein 0.9 g of lithium hydroxide and 10 ml of water were added. After stirring for 12 hours at room temperature, acidified with hydrochloric acid at 0 °C. The reacting solution was diluted with 100 ml of ethyl acetate and once washed with water. The organic layer was dried with magnesium sulfate, filtered and concentrated. The obtained residue was treated with ethyl ether and hexane to afford 2.3 g of the desired product. (white solid)

m.p. : 166 ~ 168 °C

¹H NMR(200MHz, CDCl₃) : δ 1.33(dd, 3H, *J*_{H-H}=6.4Hz, *J*_{H-F}=24.6Hz),
 3.08(brs, 1H), 3.96(s, 6H), 4.86-5.25(m, 1H),
 5.80(s, 1H), 5.89-6.07(m, 1H), 7.36-8.24(m, 5H),
 12.82(brs, 1H).

IR(KBr) ν (C=O) 1705 cm⁻¹

20 **EXAMPLE 8**

Threo *N*-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1-hydroxy-*n*-propyl)-benzenesulfonamide [Compound No. 2]

3.0g of the desired product (white solid) was obtained using the same method of EXAMPLE 7 from threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-benzenesulfonamide(3.7 g).

m.p. : 189 ~ 191 °C

¹H NMR(200MHz, CDCl₃) : δ 1.36(dd, 3H, *J*_{H-H}=6.4Hz, *J*_{H-F}=24.2Hz),
 3.0(brs, 1H), 3.96(s, 6H), 4.78-5.11(m, 1H),
 5.80(s, 1H), 5.79-5.91(m, 1H), 7.22-7.78(m, 4H),

31

8.13-8.22(m, 1H), 12.75(brs, 1H).

IR(KBr) ν (C=O) 1691 cm^{-1} **EXAMPLE 9**Erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-3-pyridinesulfonamide.

- 5 5.0 g of erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-(1,1-dimethylethyl)-3-pyridinesulfonamide was dissolved in 20 ml of trifluoroacetic acid. After stirring for 12 hours at 35 °C, the reaction solution was concentrated under vacuum. The residue was dissolved in methylene chloride and washed with NaHCO_3 solution. The organic layer was dried with anhydrous magnesium sulfate and the residue was crystallized with ethyl
- 10 acetate and hexane to afford 3.0 g of the desired product.

m.p. : 141 ~ 143 °C

 ^1H NMR(200MHz, CDCl_3) : δ 1.55(dd, 3H, $J_{\text{H-H}}=6.5\text{Hz}$, $J_{\text{H-F}}=25\text{Hz}$),

2.18(s, 3H), 4.93-5.29(m, 1H), 5.68(brs, 2H),

6.55-6.62(m, 1H), 7.43-7.50(m, 1H),

- 15 8.35-8.38(m, 1H), 8.82-8.85(m, 1H)

Crystal data of the product prepared by the above EXAMPLE 9 is the following.

Crystal Data

- | | | |
|--|---|---|
| Molecular Formula | : | $\text{C}_{10}\text{H}_{13}\text{FN}_2\text{O}_4\text{S}$ |
| Crystal System | : | Trichlinic system |
| 20 Space Group | : | P1 |
| Molecularity of inner unit lattice(Z) | : | 2 |
| $a = 8.529$, $b = 10.270$, $c = 8.528$, $\alpha = 110.09$, $\beta = 99.28$, $\gamma = 110.08$ | | |
| No. of independent diffraction data | : | 1953 |
| Final Reliancity factor | : | 6.19% |
| 25 X-ray Wave Length | : | 1.5405 |

Atomic scattering factor used to X-ray crystallography is described in the following Table 4 and stereoconfiguration of innermolecular atoms are given in Figure 2.

Table 4.

	Atoms	x	y	z	Ueq
5	S	0.63350(0)	0.56940(0)	0.37580(1)	0.205(4)
	F	0.9981(5)	0.9201(5)	0.7942(7)	0.29(1)
	N	0.4564(8)	0.5644(8)	0.2715(8)	0.27(2)
	O1	0.6198(6)	0.9893(5)	0.7386(6)	0.23(1)
	O2	0.3911(7)	0.8254(7)	0.4979(8)	0.28(1)
10	O3	0.7802(7)	0.6911(6)	0.3769(7)	0.28(1)
	O4	0.6179(7)	0.4174(6)	0.3044(7)	0.27(1)
	C1	0.6273(8)	0.6136(7)	0.5963(8)	0.19(1)
	C2	0.6479(8)	0.7545(8)	0.7121(8)	0.19(1)
	N3	0.6190(8)	0.7774(7)	0.8588(7)	0.22(1)
15	C4	0.573(1)	0.6565(8)	0.9094(9)	0.28(2)
	C5	0.561(1)	0.5174(9)	0.807(1)	0.27(2)
	C6	0.5858(9)	0.4914(8)	0.6428(9)	0.23(2)
	C7	0.7158(8)	0.9012(7)	0.8863(9)	0.21(1)
	C8	0.9037(9)	1.0076(8)	0.8095(8)	0.21(2)
20	C9	0.994(1)	1.1395(9)	0.768(1)	0.28(2)
	C10	0.4606(9)	0.9429(8)	0.6262(9)	0.24(2)
	C11	0.388(1)	1.056(1)	0.689(1)	0.40(3)
	HA	0.4615	0.6782	0.3215	0.0740
	HB	0.3448	0.4873	0.2893	0.3006
25	H4	0.5438	0.6717	1.0313	0.0542
	H5	0.5324	0.4277	0.8508	0.0636
	H6	0.5733	0.3807	0.5557	0.0222
	H7	0.7043	0.8652	0.5485	0.0480
	H8	0.8978	1.0570	0.9413	0.0785
30	H9A	0.9217	1.2086	0.7800	0.4316
	H9B	0.9996	1.0959	0.6356	0.0814
	H9C	1.1261	1.2090	0.8595	0.0846
	H11A	0.2604	1.0164	0.5974	0.1528
	H11B	0.4757	1.1654	0.6998	0.2462
35	H11C	0.3748	1.0680	0.8169	0.4053

EXAMPLE 10

Threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-3-pyridinesulfonamide

1.6 g of the desired product was obtained using the same method of EXAMPLE 9 from threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-(1,1-dimethylethyl)-3-pyridinesulfon-

5 amide (3.0 g)

m.p. : 164 ~ 165 °C

¹H NMR(200MHz, CDCl₃) : δ 1.17(dd, 3H, *J*_{H-H}=6.5Hz, *J*_{H-F}=23.9Hz),

2.16(s, 3H), 5.03-5.38(m, 1H), 5.79(brs, 2H),

6.54-6.64(m, 1H), 7.43-7.49(m, 1H),

10 8.35-8.40(m, 1H), 8.80-8.83(m, 1H)

EXAMPLE 11

Erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-3-pyridinesulfonamide [Compound No. 10]

5.1 g of the desired product (white solid) was obtained using the same method of
15 EXAMPLE 5 from 3.9 g of erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-3-pyridinesulfonamide.

m.p. : 218 ~ 220 °C

¹H NMR(200MHz, CDCl₃) : δ 1.46(dd, 3H, *J*_{H-H}=6.4Hz, *J*_{H-F}=24.9Hz),

2.04(s, 3H), 3.96(s, 6H), 4.98-5.26(m, 1H),

20 5.78(s, 1H), 6.55-6.62(m, 1H), 7.2(brs, 1H),

7.45-7.51(m, 1H), 8.60-8.65(m, 1H),

8.80-8.83(m, 1H), 13.23(br s, 1H)

EXAMPLE 12

25 Threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-3-pyridinesulfonamide [Compound No. 11]

2.9 g of the desired product (white solid) was obtained using the same method of
EXAMPLE 5 from 2.3 g of threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-3-pyridinesulfonamide.

30 m.p. : 190 ~ 192 °C

34

¹H NMR(200MHz, CDCl₃) : δ 1.28(dd, 3H, $J_{H-H}=6.4\text{Hz}$, $J_{H-F}=23.9\text{Hz}$),
 2.01(s, 3H), 3.97(s, 6H), 5.08-5.38(m, 1H),
 5.79(s, 1H), 6.49-6.60(m, 1H), 7.20(brs, 1H),
 7.46-7.53(m, 1H), 8.64-8.69(m, 1H),
 8.82-8.85(m, 1H), 13.08(brs, 1H)

EXAMPLE 13

Erythro *N*-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1-hydroxy-*n*-propyl)-3-pyridinesulfonamide [Compound No. 7]

2.1 g of the desired product (white solid) was obtained using the same method of

10 **EXAMPLE 7** from 3.0 g of erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-3-pyridinesulfonamide

m.p. : 151 ~ 153 °C

¹H NMR(200MHz, CDCl₃) : δ 1.37(dd, 3H, $J_{H-H}=6.2\text{Hz}$, $J_{H-F}=24.8\text{Hz}$),
 3.95(s, 6H), 4.11(d, 1H), 4.66-4.95(m, 1H),
 15 5.57-5.69(m, 1H), 5.78(s, 1H), 7.33(brs, 1H),
 7.46-7.53(m, 1H), 8.62-8.67(m, 1H),
 8.79-8.82(m, 1H), 12.98(brs, 1H)

EXAMPLE 14

20 Threo *N*-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1-hydroxy-*n*-propyl)-3-pyridinesulfonamide.[Compound No. 8]

0.7 g of the desired product (white solid) was obtained using the same method of **EXAMPLE 7** from 1.0g of threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-3-pyridine sulfonamide.

m.p. : 173 ~ 175 °C

25 ¹H NMR(200MHz, CDCl₃) : δ 1.48(dd, 3H, $J_{H-H}=6.3\text{Hz}$, $J_{H-F}=24.2\text{Hz}$),
 3.97(s, 6H), 4.40(d, 1H), 4.90-5.30(m, 1H),
 5.31-5.55(m, 1H), 5.82(s, 1H), 7.3(brs, 1H),
 7.49-7.55(m, 1H), 8.58-8.63(m, 1H),
 8.82-8.85(m, 1H), 13.0(brs, 1H)

EXAMPLE 15

The herbicidal effect of the compounds of the present invention was tested by the greenhouse test, the method is as followings.

Pre-emergence test

- 5 To produce a suitable preparation of active compound, 1 part by weight of active compound was mixed with 5 parts by weight of acetone, 1 part by weight of alkylaryl polyglycol ether as emulsifier was added and the solution diluted with water to the desired concentration. Seeds of the test plants are shown in normal soil and, after 24 hours, watered with the preparation of the active compound.
- 10 It is expedient to keep constant the amount of water per unit area. The concentration of the active compound in the preparation is of no importance, only the amount of active compound applied per unit area being decisive. After three weeks, the degree of damage to the plants was rated in % damage in comparison to the development of the untreated control.
- 15 The figures denote :
- 0% = no action (like untreated control)
 - 20% = slight effect
 - 70% = herbicidal effect
 - 100% = total destruction.
- 20 In this test, the active compounds(I) according to the preparation examples exhibited a better herbicidal activity against mono- and dicotyledon weeds.

EXAMPLE 16post-emergence test

- 25 To produce a suitable preparation of active compound, 1 part by weight of active compound was mixed with 5 parts by weight of acetone, 1 part by weight of emulsifier was added and the solution diluted with water to the desired concentration.

36

Test plants which had a height of 5~15 cm were sprayed with the preparation of the active compound in such a way as to apply the particular amounts of active compound desired per unit area. The concentration of the spray liquid was so chosen that the particular amounts of active compound desired were applied in 2,000 l of water / ha.

- 5 After three weeks, the degree of damage to the plants was rated in % damage in comparison to the development of the untreated control.

The figures denote :

0% = no action (like untreated control)

20% = slight effect

- 10 70% = herbicidal effect

100% = total destruction.

In this test, the active compounds (I) according to the preparation examples exhibited a better herbicidal activity against mono- and dicotyledon weeds.

15 EXAMPLE 17

Fresh-water treatment paddy submerged test

A plastic pot having a surface area of 60cm² or 140cm² was filled with a small amount of fertilizer, after then, the sterilized paddy soil of puddled state at the depth of 5-cm.

- 20 Seeds of barnyard grass, umbrella plant, dayflower, monochoria, toothcup, smartweed, and bulrush et al. and perennial nutrition body of flat-sedge and arrowhead et al., were seeded or planted in surface layer of soil, and pregerminated rice with 2-3 leaves was transplanted one root per pot at the depth of 2cm.

- After planting, the pot was watered for a day at the depth of 2cm and the
25 manufactured herbicide was spot-treated on the plant in manner similar to the field condition (4mg/pot).

Two weeks after treatment, herbicidal effect was measured by the same survey standard as that for field condition.

- It is understood that the above examples are illustrative but not limitative of the
30 present invention and that other embodiments within the spirit and scope of the invention

37

will suggest themselves to those skilled in the art.

The following Table 5 represents the formula of active ingredients of the present invention. The following Table 6~8 represents pre- and post-emergence herbicidal effect of active ingredients.

5

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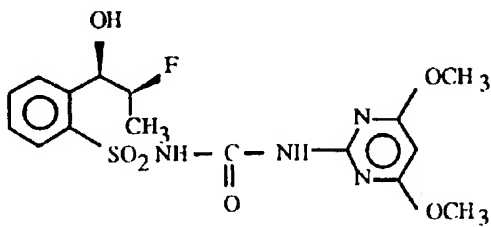
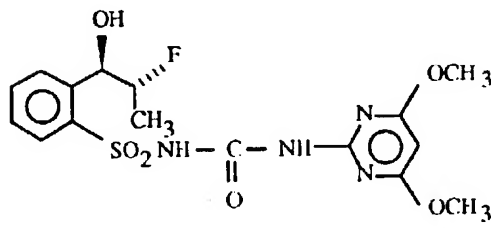
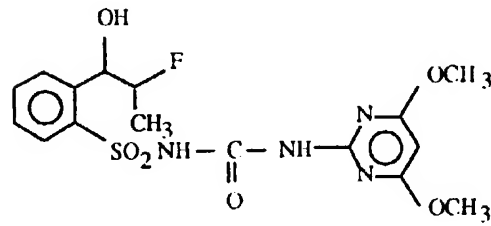
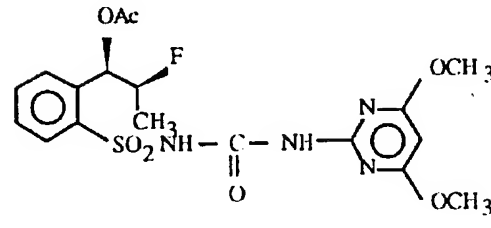
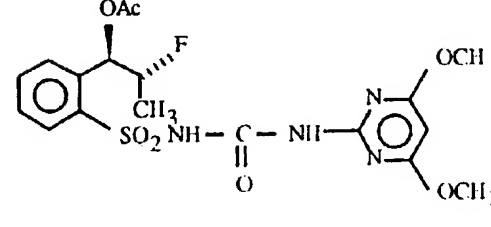
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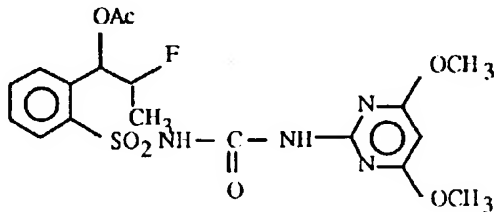
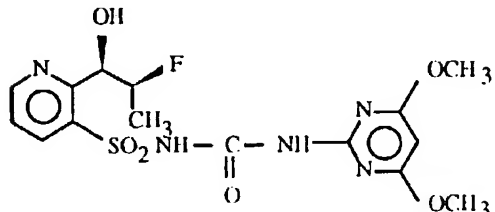
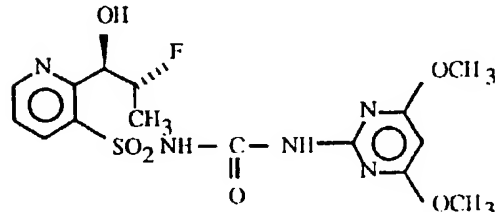
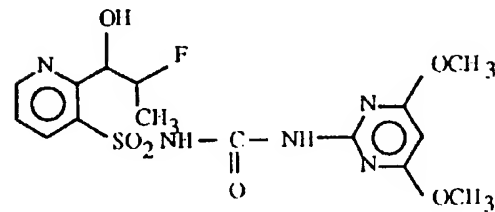
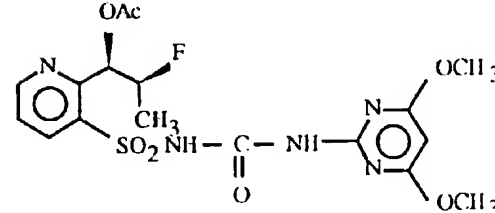
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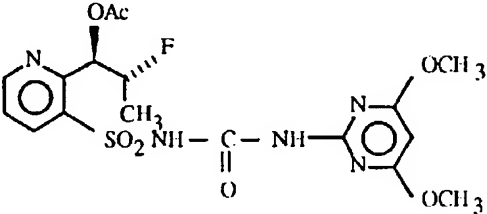
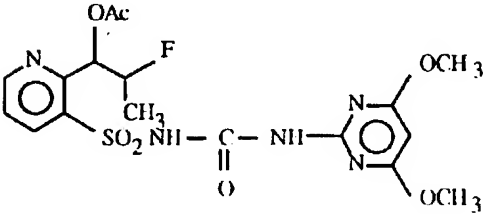
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Table 5.

Structures		Compound No.	
	erythro	1	
	threo	2	
	mixture	3	
	erythro	4	
	threo	5	

Structures	Compound No.	
	threo	6
	erythro	7
	threo	8
5 	mixture	9
	erythro	10

40

Structures	Compound No.	
	threo	11
	mixture	12

5

10

15

Table 6. PRIMARY SCREENING (PADDY SUBMERGED)-Herbicide

	Compound No.	DAT*	kg/ha	ECHOR ⁽¹⁾	SCPJU ⁽²⁾	MOOVA ⁽³⁾	CYPSE ⁽⁴⁾	SAGPY ⁽⁵⁾
5	1	2	0.0125	100	100	100	100	100
	2	2	0.0125	70	70	100	100	100
	3	2	0.0125	95	80	80	100	60
10	4	3	0.0125	95	90	100	85	100
	5	3	0.0125	70	80	70	50	95
	6	2	0.0125	85	80	80	60	75
	7	2	0.0125	100	100	100	100	100
15	8	2	0.0125	20	0	40	90	90
	9	2	0.0125	60	40	40	90	100
	10	2	0.0125	100	95	100	100	100
	11	2	0.0125	20	0	50	90	50
20	12	2	0.0125	80	30	0	100	100

(note) *DAT : Day After Treatment

(1)ECHOR : *Echinochloa crus-galli*P.BEAUUV. var. *oryzicola* OHWI. : Barnyard grass25 (2)SCPJU : *Scirpus juncoides* ROXB. : Bulrush(3) CYPSE : *Cyperus serotinus* ROTTB. : Flat-sedge(4) MOOVA : *Monochoria vaginalis* PRESL. : Monochoria(5) SAGPY : *Sagittaria pygmaea* MIQ. : Arrow head

42

Table 7. Harmful Effects Test of Herbicides*¹

DAT	g/ha	Harmful Effects of Herbicides	
		Compound No.1	Compound No.7
5	5	0	0
5	10	10	0
5	20	20	0

* ¹ transplanted rice : 5 DAT treatment after transplanting of 2 leaves rice

survey : Comparison of living body weight after herbicidal treatment

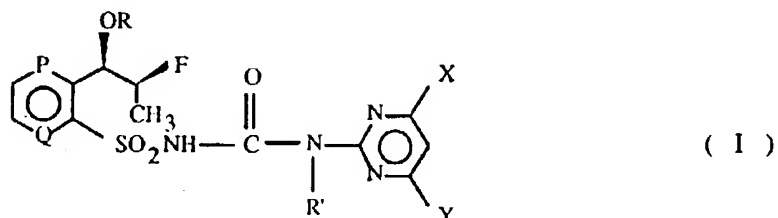
Table 8. Percentage Control for Barnyard grass

Leaf Stage	g/ha	Percentage Control(%)	
		Compound No.1	Compound No.7
1 Leaf	2.5	86	88
(6DAS)	5	95	95
	10	95	95

WHAT IS CLAIMED IS :

1. Sulfonyl urea derivatives of the following formula(I) having substituent of erythro-type stereoisomer,

5



wherein,

P and Q, as equivalent or different group respectively, are CH or N, and present as aromatic ring including P and Q as benzene or pyridine ring ;

10

R is H, $R^a - \overset{\overset{\text{O}}{\parallel}}{\text{C}} -$ or $R^a - X^a - \overset{\overset{\text{O}}{\parallel}}{\text{C}} -$ group, wherein R^a is $C_1 \sim C_4$ alkyl, $C_1 \sim C_3$ haloalkyl, $C_2 \sim C_4$ alkenyl or $C_2 \sim C_4$ alkynyl group, wherein X^a is O, S, NH or NR^a group;

15

R' is H or CH_3 group; and

X and Y are independently halogen atom, $C_1 \sim C_2$ alkyl, $C_1 \sim C_2$ alkoxy or $C_1 \sim C_2$ haloalkoxy group.

2. Sulfonyl urea derivatives according to claim 1, wherein said R is hydrogen atom or acetyl group, said P and Q are independently CH or N, and said X and Y are respectively methoxy group.
3. Sulfonyl urea derivative according to claim 1, wherein said formula(I) is erythro *N*-[(4,6-dimethoxy-pyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1-hydroxy-*n*-propyl)-benzenesulfonamide.

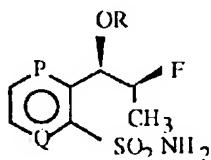
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4. Sulfonyl urea derivatives according to claim 1, wherein said formula(I) is erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-[(4,6-dimethoxy-pyrimidin-2-yl)-aminocarbonyl]-benzenesulfonamide.

5. Sulfonyl urea derivatives according to claim 1, wherein said formula(I) is erythro *N*-[(4,6-dimethoxy-pyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1-hydroxy-*n*-propyl)-3-pyridinesulfonamide.

6. Sulfonyl urea derivatives according to claim 1, wherein said formula(I) is erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-[(4,6-dimethoxy-pyrimidin-2-yl)aminocarbonyl]-3-pyridinesulfonamide.

7. Intermediate compounds of the following formula(II) having erythro-type,



(II)

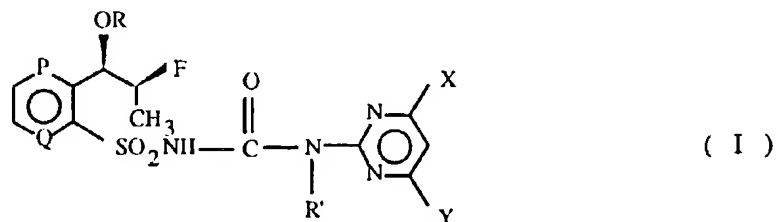
wherein, R,P and Q is respectively as defined in the above claim 1.

8. Intermediate compound according to claim 7, wherein said formula(II) is erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-benzenesulfonamide.

9. Intermediate compound according to claim 7, wherein said formula(II) is erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-3-pyridinesulfonamide.

10. Herbicidal compositions including sulfonyl urea derivatives of following formula (I) as an effective component,

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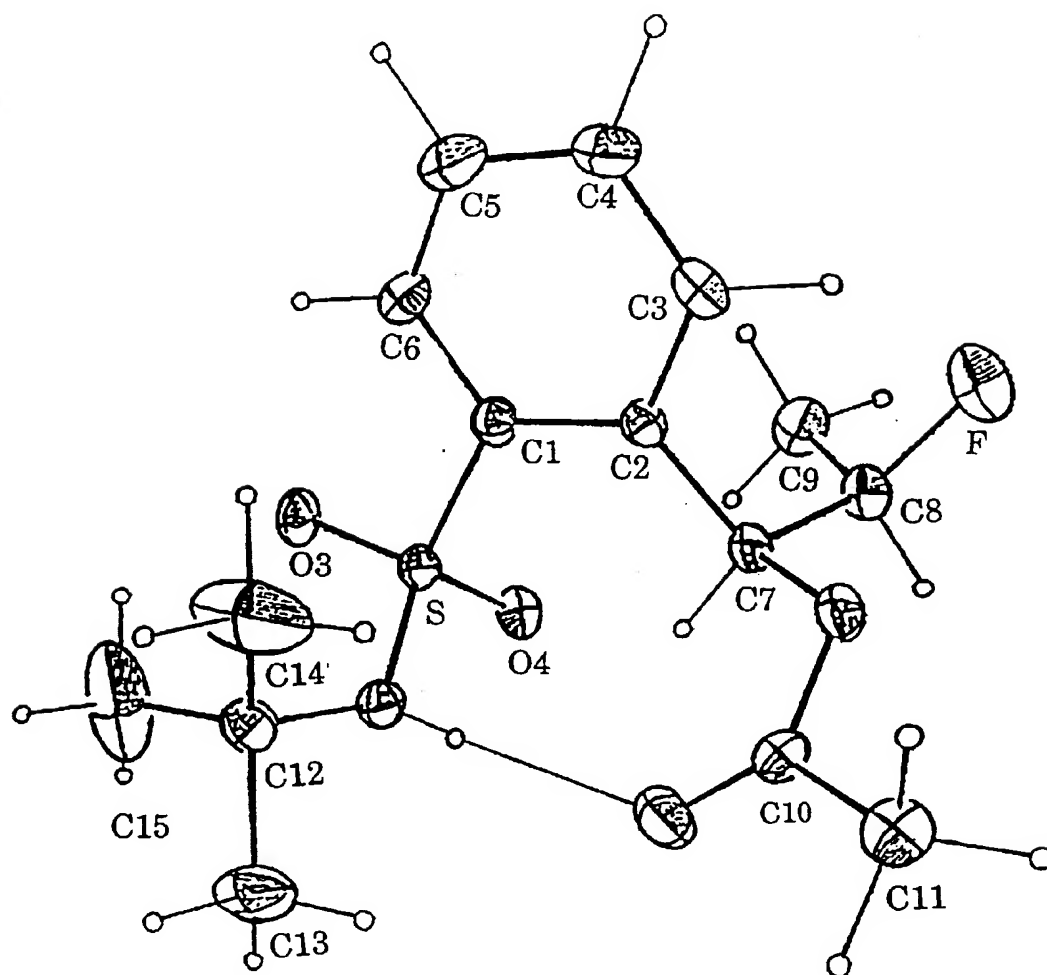


wherein P, Q, R, R', X and Y are respectively as defined in the above claim 1.

11. Herbicidal composition according to claim 10, wherein said sulfonyl urea derivatives of formula(I) is that R is hydrogen atom or acetyl group; Q is CH; P is CH or N; R' is hydrogen atom; and X and Y are respectively methoxy group.
12. Herbicidal composition according to claim 10, wherein said sulfonyl urea derivatives of formula(I) is erythro *N*-[(4,6-dimethoxy-pyrimidine-2-yl)-aminocarbonyl]-2-(1-hydroxy-2-fluoro-*n*-propyl)-benzenesulfonamide.
13. Herbicidal composition according to claim 10, wherein said sulfonyl urea derivatives of following formula(I) is erythro *N*-[(4,6-dimethoxy-pyrimidin-2-yl)aminocarbonyl]-2-(1-hydroxy-2-fluoro-*n*-propyl)-3-pyridine-sulfonamide.

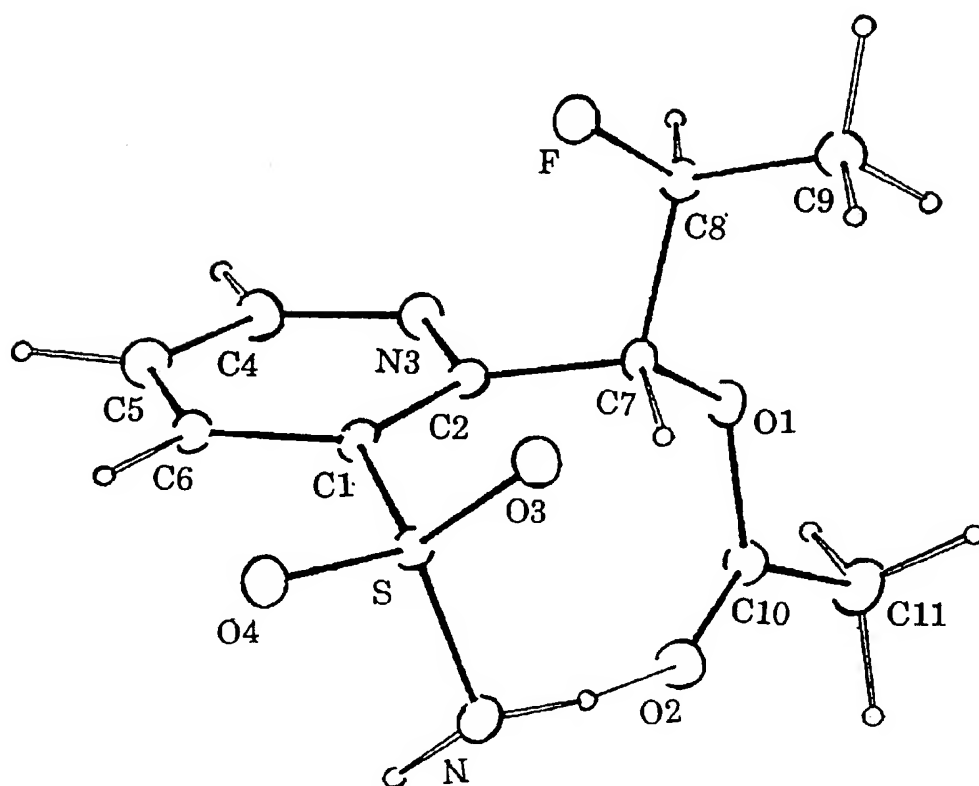
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FIG. 1



WEST

FIG. 2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR 94/00147

A. CLASSIFICATION OF SUBJECT MATTER

IPC⁶: C 07 D 239/42, 401/14, 213/73; C 07 C 311/29; A 01 N 47/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁶: C 07 D 239/42, 401/14, 213/73; C 07 C 311/29; A 01 N 47/36

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 044 807 A2 (CIBA-GEIGY AG) 27 January 1982 (27.01.82), claims 1, 27, 29; (cited in the application).	1, 7, 10
A	US 4 443 245 A (MEYER et al.) 17 April 1984 (17.04.84), abstract; (cited in the application).	1, 10
A	EP 0 240 216 A1 (SUMITOMO CHEMICAL COMPANY) 07 October 1987 (07.10.87), page 3, lines 31-33.	1, 10
A	US 4 532 328 A (KLESCHICK) 30 July 1985 (30.07.85), column 1, lines 12-15.	1, 10
A	EP 0 512 953 A1 (CIBA-GEIGY AG) 11 November 1992 (11.11.92), abstract.	7, 8

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

04 August 1995 (04.08.95)

Date of mailing of the international search report

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Name and mailing address of the ISA/ AT

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Telephone No. 1/5337058/31

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/KR 94/00147

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